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Adhesives: Test Method, Group Assignment, and Categorization Guide for High-Loading-Rate Applications – History and Rationale

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NOTICES

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by Robert Jensen, David Flanagan, Daniel DeSchepper, and Charles Pergantis
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Coatings, Corrosion, and Engineered Polymers Branch (CCEPB)*
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14. ABSTRACT
This report provides the development history and rationale for the standard process description ARL-ADHES-QA-001.00 Rev 1.0, *Adhesives: Test Method, Group Assignment, and Categorization Guide for High Loading Rate Applications*, by the Adhesives and Informatics Team, Coatings, Corrosion and Engineered Polymers Branch, US Army Research Laboratory.

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1.0 Purpose

This report provides the development history and rationale for the standard process description (SPD) ARL-ADHES-QA-001.00 Rev 1.0, *Adhesives: Test Method, Group Assignment, and Categorization Guide for High-Loading-Rate Applications*, by the Adhesives and Informatics Team, Coatings, Corrosion and Engineered Polymers Branch (CCEPB), US Army Research Laboratory (ARL).

2.0 Scope

This SPD fulfills partial requirements for the CCEPB to qualify for International Organization for Standardization 9001:2008 certification.

Disclaimer: This report contains ARL-originated studies containing advice and recommendations. The "History and Rationale" of the title is included as a consideration to future researchers.

Figure 1 shows the property assignment regions for adhesive group categories specified in *Adhesives: Test Method, Group Assignment, and Categorization Guide for High-Loading-Rate Applications*, ARL-ADHES-QA-001.00 Rev 1.0.[1] The assignment regions can be defined by a plot of maximum strength (S_{max}) versus displacement complete failure (d_{failure}) as measured from standardized single-lap-joint tests per ASTM D1002 under quasi-static loading conditions at room temperature (RT).[2] Figure 2 shows a global plot of S_{max} versus d_{failure} with the inclusion of 894 experimental data test points taken at and by ARL for various adhesive materials. Figure 3 provides a more-detailed data representation with respect to the adhesive material types. The intended ARL focus of testing these adhesives has primarily been for bonding armor assemblies. The global response to ballistic loading for a number of these adhesives has been observed and evaluated by ARL researchers.

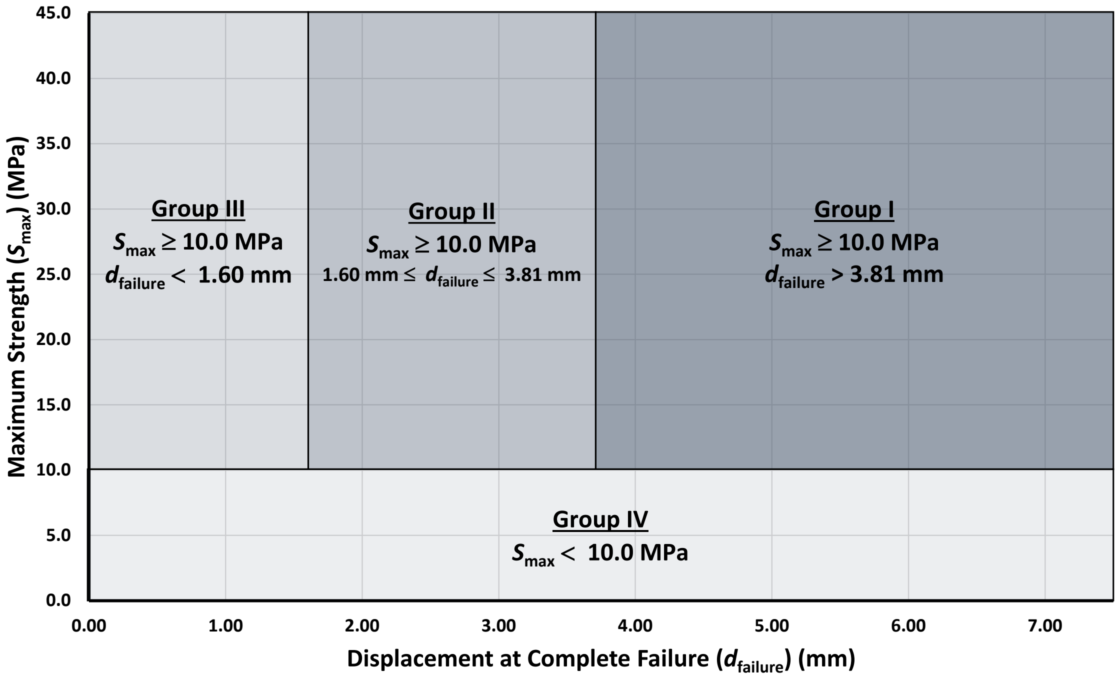

Fig. 1 Adhesive groups based upon single-lap-joint performance (S_{max} and $d_{failure}$) at RT (dry conditioning)

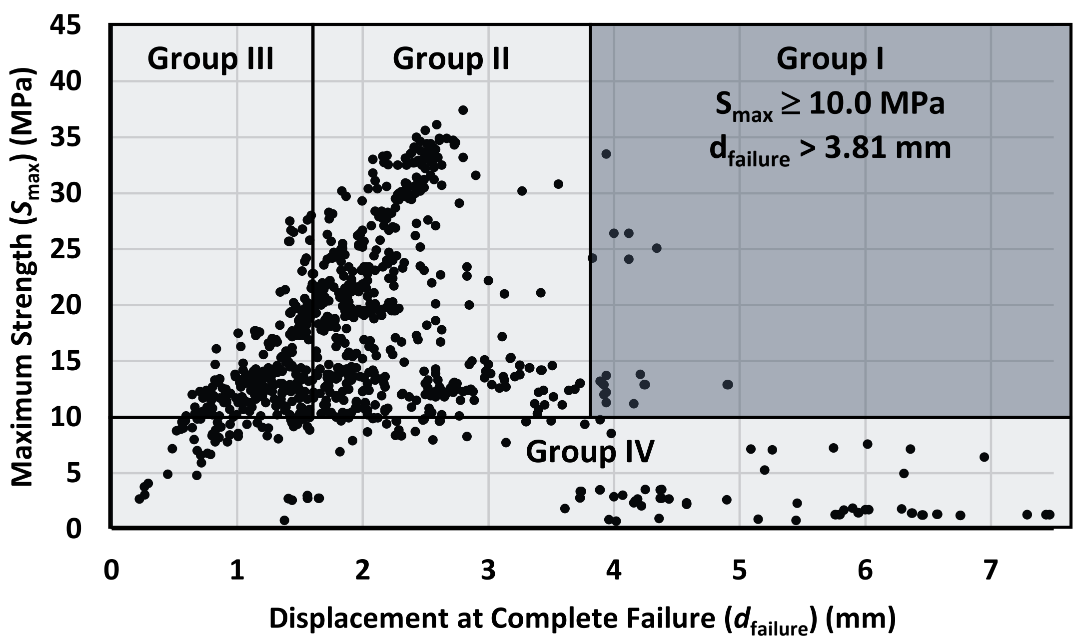

Fig. 2 ARL experimental population of adhesive groups based upon S_{max} and $d_{failure}$ single-lap-joint performance at RT (dry conditioning)

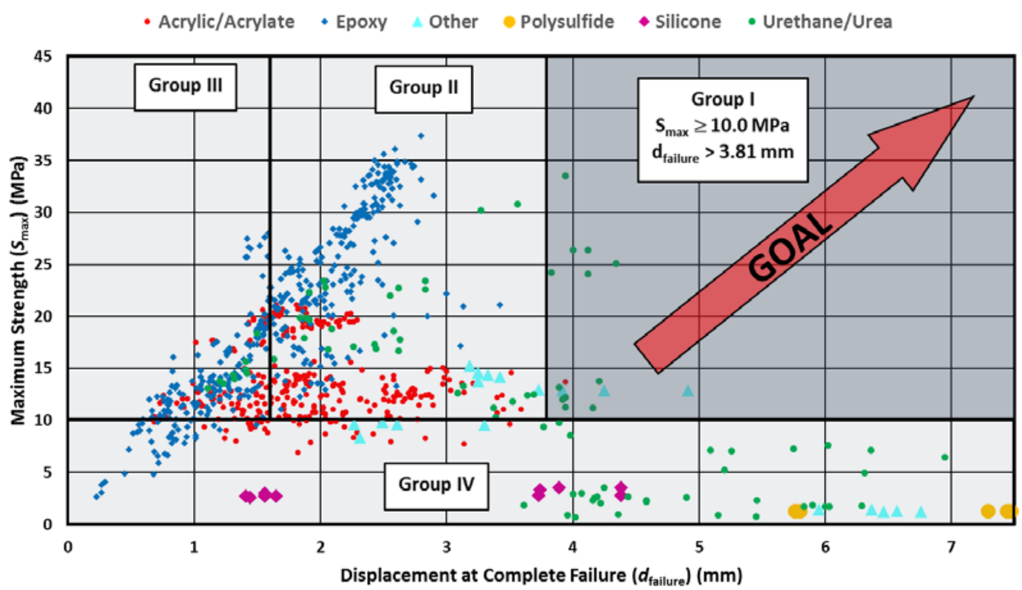

Fig. 3 Detailed ARL experimental population of single-lap-joint performance showing adhesive chemical classifications. Dry sample conditioning tested at normal RT and humidity conditions (1.62-mm-thick 2024 T3 aluminum substrates).

2.1 Adhesive Categories

2.1.1 Group I Category Adhesives (Adhesives for High-Loading-Rate Environments)

Group I adhesives represent a performance region where increases in ballistic damage tolerance occur with respect to survivability of the bondline. This is a qualitative assessment based on the global performance of the bonded armor assembly against the test threat, the size of the damage area, the damage modes of the constituent armor materials, and if the adhesive bondline will withstand multiple impacts (i.e., the strike face and backing plate bond remains intact). The further hot/wet and elevated temperature requirements specified in ARL-ADHES-QA-001.00 are screening checks to minimize potential longer-term service durability issues with an upfront minimal effort in testing. ARL-ADHES-QA-001.00 conveys the empirical observations and experience of ARL researchers in using adhesives to bond armor assemblies in terms of quasi-static performance metrics using a well-established academic and industrial test geometry configuration. The eventual "goal" for adhesives for armor applications is to develop, test, and evaluate a system able to withstand maximum strength and deflection much greater than 10.0 MPa and 3.81 mm, respectively, as shown in Fig. 3.

2.1.1.1 Experimental and Modelling Challenges

The loading conditions experienced by ground combat vehicles during high-strain-rate/high-stress (ballistic) events are complex.[3–13] From the Army's call for proposals to establish a Collaborative Research Alliance focused on Materials in Extreme Dynamic Environments (MEDEs), the fundamental problem is "the lack of understanding of the physical phenomena at multiple scales that govern high-stress and high strain-rate material performance resulting from the paucity of validated linkages between experimental and computational research tools at critical length and time scales."[14] Specifically, the MEDE proposal guidance outlined the following major gaps in the current state of the art:

- A limited ability to relate materials chemistry, structure, and defects to materials response and failure under extreme conditions.
- An inadequate ability to predict the roles of materials structure, processing, and properties on performance in relevant extreme environments and designs.
- The lack of experimental capabilities to quantify multiscale response and failure of materials under extreme conditions.

2.1.1.2 Variable High-Loading-Rate Environments

Lightweight armor configurations are constantly evolving as new threats are encountered.[15–21] Co-evolution of predator and prey species occurs in nature.[22–28] Historically, threat and protection schemes engaged in human combat are also continuously co-evolving, such as armor and antiarmor development. Liddel Hart pointed out that in 1940 the use of a propelled armored offensive was "a concept as revolutionary as the use of the horse, the long spear, the phalanx, the flexible legion, the 'oblique order', the horse-archer, the longbow, the musket, the [artillery] gun".[29]

2.1.1.3 Minimal Linkages to Academia and Industry

Little information pertaining to armor configurations exists in the open literature. Literature that does exist is related to generic (unclassified) armor configurations matched against unclassified threats, such as 7.62-mm fragment-simulating projectiles and so on. Typically, only the global response of the armor package/assembly is observed and evaluated. Regardless of the material studied (ceramic, metal, composite, adhesive, etc.), trends are implied, but distinct constitutive properties are seldom determined,[30–32] whereas useful generic studies are challenging to scale as the momentum and impact energies of the ballistic event increase in magnitude.

Armor specifications are typically based upon performance, while aerospace adhesive specifications define precise material properties using standardized and accepted testing protocols. Aerospace specifications are well-known and implementable by adhesive formulators. Armor specifications, including spall liners, aluminum, and rolled homogeneous armor steel, are restrictive in terms of material composition and performance.[33–36]

The absence of high loading rate–derived adhesive specifications can lead to borrowing from aviation, which may not provide adequate performance in high-loading-rate regimes.

2.1.1.4 Comments on Ballistic Testing of Adhesively Bonded Armor Assemblies

Judgments on the performance ratings of individual armor assembly constituents, including the adhesive, are typically tied to the global performance of the entire armor package. A high-performance rating from ballistic testing does not guarantee that the adhesive will maintain the characteristics as the threat and armor configuration vary. Likewise, poor performance in a single test configuration does not always guarantee that the adhesive will not be suitable in alternative armor designs.

2.1.2 Group II, III, and IV Category Adhesives

The experimental data points plotted in Figs. 1–3 show the highest population densities in Groups II, III, and IV. Groups II and III are attainable by current aerospace-grade bonding adhesives, and Group IV performance metrics can be achieved by aerospace-grade sealants. Groups II, III, and IV are realistic performance criteria for adhesives that have previously scaled through Department of Defense (DOD) technology-readiness-level progressions into full commercial availability. In contrast, Group I is sparingly populated with very few experimental data test points for a relatively few adhesives that are not at commercial acceptance levels. The continual evolving and variable nature of armor protection schemes will ensure a multitude of adhesive bonding schemes needed to meet Group I requirements. This armor configuration variability and relatively mild upper-service temperature requirements could provide the impetus for adhesive formulators to probe ground vehicle applications for product expansion, particularly where non-DOD commercial opportunities exist. This could potentially lead to adhesive advancements past the development plateau of aerospace, as portrayed in Fig. 4.

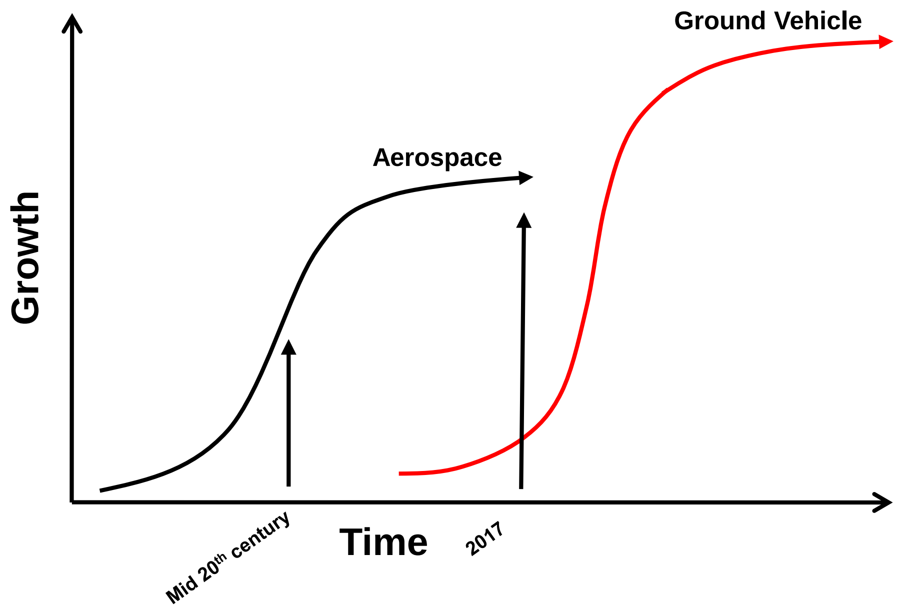

Fig. 4 The bonding requirements for adhesives in ground vehicle applications require technological development past aviation benchmarks

Supplemental commentary is reported in the following appendix sections describing technological growth progression and a brief history of high-performance adhesives from the aerospace industry.

3.0 Policy

Not applicable.

4.0 Responsibilities

Not applicable.

5.0 Requirements

Not applicable.

6.0 Terms and Definitions

Not applicable.

7.0 Records

Not applicable.

8.0 Appendix A. Innovation vs. Invention

Knowledge translation progresses through 3 stages: discovery, invention, and innovation.[37,38] Discovery is the identification of new knowledge and is traditionally brought into light through mechanisms such as peer-reviewed academic papers. The invention is the embodiment, or working demonstration, of the discovery into practice. Innovation is the refinement of the invention to a sufficient stage of development to bring it to the commercial market.

Joseph Schumpeter (1883–1950) adapted the phrase "Creative Destruction" in his theories of economic development.[39–41] The variant phrase "Disruptive Technology", by Joseph Bower and Clayton Christensen, gained popularity in the mid-1990s.[42] However, Schumpeter's economic theories remain influential to modern scholars.[43]

A transistor is a semiconductor device used to control and amplify electrical currents and is a model example contrasting the following invention versus innovation stages of technology development.

- The invention of the transistor was credited to John Bardeen, Walter Brattain, and William Shockley while working for Bell Telephone Laboratories in 1947. Efforts to invent a practical transistor were the accumulation of intense war-driven needs for enhanced radar performance. Bardeen, Brattain, and Shockley were awarded the 1956 Nobel Prize in Physics for their invention.[44]

- While the invention of the transistor in 1947 represented a tremendous scientific advancement, there were still many practical considerations that were yet to be developed to successfully transition the technology into commercial industry.[45–48]

- Gordon K Teal represents the "innovator" in the history of transistor technology. Teal was a former Bell Labs employee who began working for Texas Instruments in 1953. Teal overcame the performance limitations of Bell Labs' germanium-based transistor design by developing a method to grow large single-crystal silicon as the semiconductor material. Texas Instruments was capable of mass producing the new silicon transistor design for the first successful transistor radio to progress beyond the prototype stage, the Regency TR-1, in 1954.

Innovation is the successful implementation of creative ideas within an organization.[49] According to Joseph F Engelberger, the "father of robotics", innovation requires 1) recognized need, 2) competent people with relevant technology, and 3) financial support.

Innovation also carries very high failure rates. Failure leads to loss in morale, increased cynicism, and resistance to change. Erik Brynjolfsson (Massachusetts Institute of Technology's Sloan School) basically states that industrial use of newer innovative technology occurs at higher levels once the existing management infrastructure exits the workforce.[50,51]

9.0 Appendix B. Technological Development Curves

While Schumpeter provided the initial concept that innovation was the driving force for economic growth, it was W Rupert Maclaurin, Department of Economics and Social Science at the Massachusetts Institute of Technology in the 1940s and 1950s, who first provided an analytically quantitative "linear model of innovation".[52] Prior to the Second World War, traditional economic theory reasoned that growth was simply related to the ability to increase available production capacity. Maclaurin systematically and rigorously studied "technological progressiveness" for a broad range of industries, including chemical, photographic, aviation, oil, radio and television, electric light, automobile, paper, steel, food processing, cotton and textiles, coal mining, and housing assembly, and derived the following "series of measurements" to track technological innovation for his linear model: "Linear model of innovation: Pure science to Invention to Innovation to Finance to Acceptance".[52]

Many nonlinear recursive models have been proposed since Maclaurin's initial linear growth theory to meet the complexities of specific industries.[53]

The "S-curve", shown in Fig. B-1, was conceived in the early 1970s by Richard Foster while working as a business consultant for McKinsey and Co. in New York.[54–56] The primary advantage of the S-curve is that it represents a model, of growth versus time, that is easy to comprehend.[54,57]

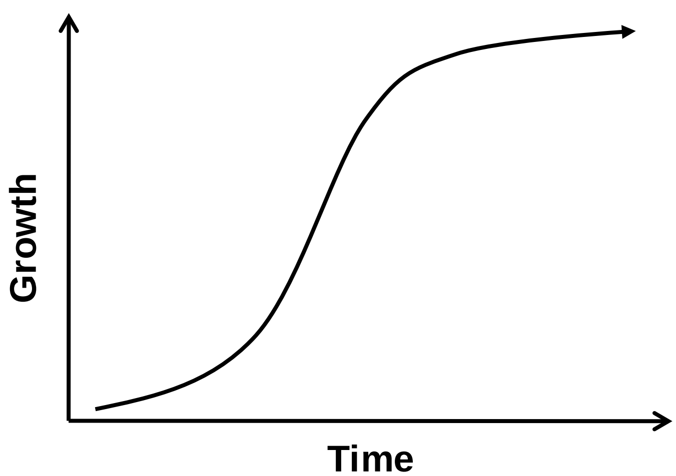

Fig. B-1 The "S-curve"

Some of the advantages of the S-curve include the following:

- Ease in evaluation of the different stages of technology
- Indicator of the need to shift when gains in growth decline
- Provides motivation to be at the forefront of new technology

- Reduces the chances of hasty rejections of emerging technology

Some of the disadvantages of the S-curve include the following:

- Does not indicate how large the gains generated by the emerging technology will be
- Does not precisely guide business managers with respect to the timing of transitioning the shift from old to new technology
- The S-curve is a generalization, which may or may not fit to specific industries.

Research efforts to mathematically quantify the S-curve are ongoing, continually.[58–61]

The actual invention stage and process of a technological growth curve, while significant, is a relatively small factor in determining the success of a new product. Inventors who more fully understand the broader growth process of technology and who are more willing to escort their invention through licensing and potential commercialization in an advisory role seem to have a better chance at bridging the gap between invention and innovation.[62] Braunerhjelm and Svensson[62] verified Schumpeter's assertion that the invention and innovation stages of technology growth are separate through a statistical study of Swedish patents. It was found that the success rate of the invention was actually lower if the inventor also assumed ownership and leadership during the innovation stage. However, true entrepreneurs who drive the innovation stage clearly benefitted when the inventor was able to assist in a supportive role, primarily to adapt the technology to specific customer needs and to reduce uncertainty.

Philibert provides a comprehensive approach to understanding the complexities in the relationships between invention, innovation, and the eventual diffusion of the new technology into the commercial marketplace at the international level in efforts to reduce global CO_2 emissions.[63] It seems to be clearly understood that the invention of new technologies as alternative energy sources is only a partial solution to curbing the rise of atmospheric CO_2 levels.

It is also known that research and development managers at corporate and government levels are intimately connected with the success or failure of new inventions.[64–66] Specifically, government lead research is in a position to absorb a greater amount of risk than corporate counterparts. Government-sponsored technical standards can provide motivation for private companies to progress from the invention to innovation stages.[65] However, it is also cautioned that government-sponsored technical standards that "do not endure" can also impede innovation.[65]

10.0 Appendix C. Development History of Aviation Adhesives

10.1 Norman de Bruyne and Aero Research Ltd

Aviation material property requirements are dominated by "strength and stiffness", which have been well-defined for the commercial adhesive industry since the middle of the 20th century:

- Aviation is a very mature industry, and the correlations between materials properties with processing, performance, design, structure, and manufacturing that have been studied extensively.[67]
- Modern adhesives with properties specifically tailored for aircraft fabrication were patented in Great Britain in the 1930s and in the United States in the 1950s.[68–70]
- Literature sources related to the performance of aircraft adhesives date at least to 1943.[71]

Modern aviation adhesives (and composites) owe their existence to the pioneering work of Norman Adrian de Bruyne in the 1930s through the 1950s.[72–74] De Bruyne earned his master's and doctoral degrees from Trinity College at the University of Cambridge studying electrical and radioactive field emission. De Bruyne had a passion for aviation and obtained his pilot's license in 1929. "He was totally dissatisfied with the complacency shown in aircraft design during the late 1920s and early 1930s, and was convinced he could do a lot better."[72]

De Bruyne formed The Cambridge Aeroplane Construction Company in 1931, which became Aero Research Limited (Duxford, Cambridge) in 1934. Aero Research Ltd was responsible for most of the initial ground-breaking inventions that aviation adhesives and composites were founded on, including the following:

- Invented Gordon Aerolite composite, which used a phenol-formaldehyde matrix and flax roving reinforcement.
- Invented Aerolite urea-formaldehyde adhesives for laminating and bonding wood. This adhesive was used to construct the laminated plywood Airspeed Horsa glider and de Havilland Mosquito.
- Invented sandwich honeycomb composite structures.
- Invented poly(vinyl formal) – phenol-formaldehyde adhesive (Redux 775) for the first metal-to-metal bonding in aircraft (de Havilland Sea Hornet).
- Invented modern film adhesives.

- Educated and introduced a much broader commercial audience to the benefits of adhesive bonding through teaching annual “summer schools” at Cambridge University in the postwar years.

De Bruyne and the technical staff at Aero Research Ltd were also innovators. While phenol and urea-formaldehyde chemistry dates to the early 1900s,[75,76] it was Aero Research Ltd that modified the chemistries and processing techniques that innovated their use for aviation applications.

10.2 Maturation of Redux 775

The advances in aviation adhesives pioneered by Norman de Bruyne and Aero Research Ltd in the 1930s and adopted by de Havilland in the 1940s were possible because the engineering properties required were already known.

From Kinloch’s memoir of de Bruyne:

- “De Bruyne became convinced that there was considerable scope for the introduction of novel designs and materials in aircraft structures, especially because it seemed that anything other than a biplane was regarded as un-English and not really practicable by the current aircraft design engineers.” [72]
- De Bruyne set about designing and constructing the Snark[73] in the early 1930s.
- De Bruyne was able to construct the Snark as a monoplane using lightweight stressed plywood, laminated with phenol-formaldehyde resin, as the fuselage and wing material.
- The design was so advanced that the Royal Aircraft Establishment (RAE) initially “dismissed the whole design concept and stated that it could not issue a certificate (so the aircraft could be legally flown) for such a lightweight structure, because its light weight must imply an inadequate strength”.
- The Snark design was approved by the RAE on June 21, 1934, following full-scale destructive testing of the fuselage structure.
- Kinloch states that de Bruyne based his design of the Snark on “Prager’s analysis of plastic failure”[77] and “Wagner’s tension field analysis”.[78]

The lessons learned from the Snark subsequently led de Havilland to use Aerolite urea-formaldehyde plywood bonding in the Mosquito[73] poly(vinyl formal) – phenol-formaldehyde adhesive (Redux 775) metal-to-metal bonding in the Sea Hornet[73] and the transition of adhesive bonding into commercial aviation with the

Dove.[79] By the end of the Second World War the basic correlations between fundamental quasi-static adhesive mechanical properties and the full structural response of aircraft were known, and the connection between performance requirements and formulation had essentially been bridged.

Although Aero Research Ltd was acquired by Ciba in 1947, Redux-type adhesives are currently qualified for aircraft production and sold through Hexcel.[80]

10.3 Increased Service Temperature Requirements

The need for higher service temperatures was a primary factor in driving adhesives for aviation applications beyond the initial phenol-formaldehyde base chemistry established by Aero Research Ltd. However, their exact histories are much more difficult to trace through academic literature and patent references. Wikipedia states that resin formulation based upon epichlorohydrin was first reported in 1927, and modern bisphenol-A epoxy resins were invented by Pierre Castan (Switzerland) and Sylvan Greenlee (United States) in 1937.[81] The Wikipedia statements were not verified directly, though patents for Castan[82] and Greenlee[83] issued at later dates indicate that it is possible that they were involved with epoxy synthesis.

Likewise, the origins of epoxy film adhesives are equally obscure in the literature and patent archives, although Higgins reports the use of American Cyanamid (Cytec) FM 1000 for bonding in the Boeing 727 in 1963.[84] A large number of representative epoxy adhesive patents can be found from the 1950s, 1960s, and 1970s.[85–87]

The possible origins of bismaleimide (BMI) and cyanate-ester-resin-based adhesives are even more obscure in the patent literature.[88,89] The academic literature for BMI and cyanate-ester-based adhesives becomes more widespread in the 1990s although not approaching the number of publications for epoxy adhesives.[90,91]

10.4 Plateaued Development

The drive by the commercial aviation industry for lighter aircraft has resulted in a steady increase the use of composite structures since the mid-1970s.[84] The use of adhesives and composites should scale with each other.

- The McDonnell Douglass MD-80 used less than 5% composite structure by weight in 1980. The current Boeing 787 uses approximately 50% composite structure by weight.
- Additional metal-to-metal bonding also exists in aircraft, such as bonded reinforcement joints and struts, so the percentage of adhesive bonds used probably scales greater than the percentage of composite used.

This increasing use of adhesives in aircraft since the 1970s is based upon chemistry that in some cases is decades old and has not translated to the continual development of new adhesive formulations or chemistries. Results from a market survey of the adhesives and sealants industries in 2008 revealed the following:

- The market survey reported profiles for 434 adhesive companies.
- The corporate trends seemed to point toward expanding production in the BRIC (Brazil, Russia, India, and China) nations.
- Adhesive industry corporate news was dominated by mergers and acquisitions. The market survey acknowledged that the adhesives market is very dynamic.
- For 2008, 255 recent product innovations/introductions were listed but only one was aerospace-related: "Huntsman Advanced Materials Unveils New Aerospace Adhesives".
- New developments in solvent-free and environmentally friendly adhesive technology appears as most prevalent product innovation.[92]

By 2008 the technological development of aviation adhesives were certainly well within the upper plateau of growth potential based on a simple S-curve analysis, as shown in Fig. C-1.

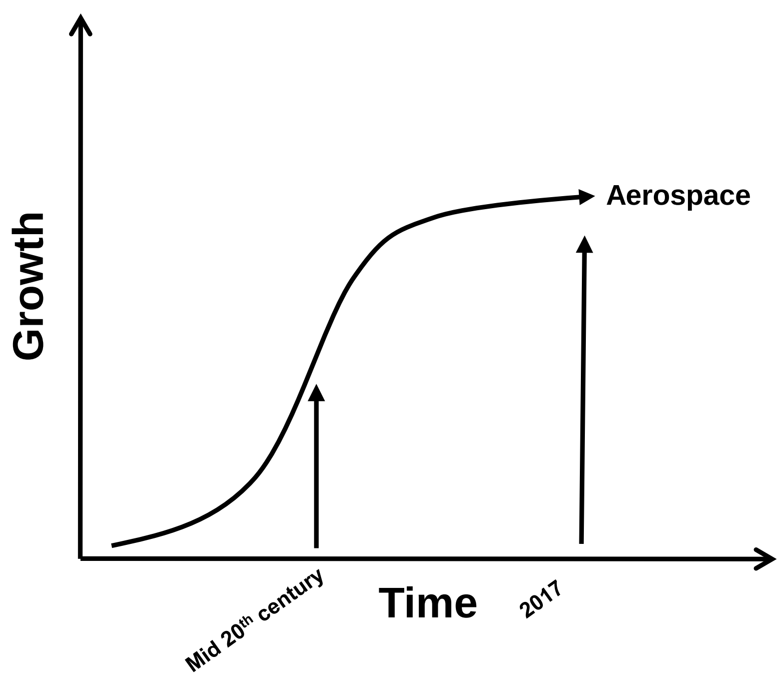

Fig. C-1 The "S-curve" for aerospace adhesives

11.0 Acknowledgments

Further contributions to the information contained in this SPD are included in the references.[93–97]

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List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
BMI	bismaleimide
BRIC	Brazil, Russia, India, and China
CCEPB	Coatings, Corrosion and Engineered Polymers Branch
d_{failure}	displacement complete failure
DOD	Department of Defense
MEDEs	Materials in Extreme Dynamic Environments
RAE	Royal Aircraft Establishment
RT	room temperature
S_{max}	maximum strength
SPD	standard process description

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